

Dedicated to the Anniversary of Academician Irina Petrovna Beletskaya

New Concepts of Colloid Chemistry: Nano-Adsorbent as a Solvent Component and Adsorption Protomicelle

Academician A. I. Rusanov^{a,b,*}, T. G. Movchan^a, and E. V. Plotnikova^a

Received December 6, 2022; revised March 16, 2023; accepted March 23, 2023

Abstract—Large molecules of dyes or other substances can act as nano-adsorbents in aqueous surfactant solutions and, being coated with surfactant molecules, they resemble surfactant micelles with a solubilizate. These micelle-like particles were called protomicelles (or, more precisely, adsorption protomicelles, as in this paper). Their formation does not require a critical micelle concentration (CMC) and begins immediately when a surfactant is added to a solution. In this spectrophotometric study of Nile red (NR) in aqueous solutions of nonanoic acid (NOA), the first case where protomicelles were more important than micelles was demonstrated. It was shown that NR solubilization in both pre-micellar and micellar solutions proceeds through protomicelles rather than through NOA micelles. In the theoretical part of the paper, on the basis of the chemical potential of the nano-adsorbent, it was proved that the addition of a surfactant to a solution always increases the solubility of the nano-adsorbent. The dependence of adsorption on the curvature of the nano-adsorbent surface was considered, and it was shown that the adsorption equations for flat surfaces are applicable to curved surfaces with high accuracy.

Keywords: Nile red, nonanoic acid, surfactant, micellization, solubilization, proto-micelles, nano-adsorbent

DOI: 10.1134/S0012501623700100

The concepts of nano-adsorbent and protomicelle were introduced in our publications [1, 2]. In this study, they are explained and specified using both new considerations and experimental data. We are pleased to dedicate this work to the anniversary of Academician Irina Petrovna Beletskaya, the queen of Russian organic chemistry!

Let us start with the nano-adsorbent. It is known that an adsorbent is often ground before experiments. It may seem that by grinding a material down to a nano-size, one already gets a nano-adsorbent, and here you are! You may continue your work. On the one hand, this is actually so, but the matter is not just about adding the sacral prefix “nano” to a term (the word “nano-adsorbent” is not new, but it is usually misused), but about a crucial change in the thermodynamic approach. A usual adsorbent is one more macroscopic phase, and adsorption takes place at the

interface between this phase and the solution. In other words, a usual adsorption system is always heterogeneous. If the size of an adsorbent particle is so small that it becomes a participant of Brownian motion, the nano-adsorbent is an equal component of the solution, and the system becomes homogeneous. “Homogeneous” means uniform; if we imagine an observer who sits at some point of the solution and monitors some property (say, density), we will get the same result for all solution points over a period of time sufficient for averaging. However, the result of this imaginary experiment would change if the center of mass of one of the particles is fixed. It immediately becomes the center of a new phase no matter how small the particle is, and the system should be classified as heterogeneous.

Like any solution, an adsorbent nano-particle has the chemical potential μ (this notion is also applicable to dispersed particles [3]). It depends on the particle size and shape; therefore, for an adsorbent obtained by grinding, a description in terms of the chemical potential becomes very complicated. However, the situation can be substantially simplified if the role of the nano-adsorbent belongs to a different substance. In this case, all nano-adsorbent particles are identical and are molecules of this substance. The moving solution par-

^a*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia*

^b*Saint Petersburg State University, St. Petersburg, 119034 Russia*

**e-mail: airusanov@mail.ru*

ticles interact with one another and form associates, but this resembles adsorption if one molecule can bind many other species present in the solution. This situation requires a large difference between the particle sizes, and we should assume that nano-adsorbent molecules are much larger than the adsorbate species.

Now look at the expression for the chemical potential of a molecule of solution component i given by statistical mechanics:

$$\mu_i = \mu_i^0 + w_i + kT \ln a_i + kT \ln \Lambda_i^3, \quad (1)$$

where μ_i^0 is the chemical potential of a molecule with the center of mass at rest in vacuum, w_i is the work for transfer of a molecule from vacuum to a certain point within the solvent (not necessarily a pure substance), a_i is the activity of component i (taking account of the interaction with all particles except the solvent), Λ_i is the de Broglie wavelength for one molecule of component i (a quantity related to the statistical sum of translational motion and depending only on temperature), and kT has a usual meaning. As applied to a nano-adsorbent, the expression in the right-hand part of (1), except for the last term, is the chemical potential of a molecule with the center of mass at rest; hence, it acts as a usual adsorbent. Therefore, it is possible to rely on the theory of adsorption, with known equations (such as the Langmuir equation) and approaches, which has been fairly well-developed to date. Any mixture of substances, except for the nano-adsorbent, can serve as the solvent. Evidently, the transfer of a nano-adsorbent molecule from vacuum to the solvent may be accompanied by spontaneous adsorption of some solvent components, which decreases the work w_i in expression (1):

$$w_i = w_i^0 - \sum_j u_j n_j. \quad (2)$$

Here w_i^0 is the w_i value in the absence of adsorption, u is the work for detachment of an adsorbate molecule from the adsorbent surface, n is the number of adsorbate molecules, subscript j numbers adsorbates if there are several of them.

The number n_{j0} of adsorption sites per unit surface area of the adsorbent is one of the most important notions of the Langmuir theory; but this theory refers to flat surfaces. Meanwhile, the surface of a nano-adsorbent particle cannot be actually regarded as flat; therefore, the applicability of the Langmuir equation to nano-adsorbents requires estimation of the error. We will do it. Let a nano-adsorbent particle be spherical and have the radius R and let an adsorbate particle (for simplicity, we take that there is only one adsorbate) have the volume v and the length d along the perpendicular to the surface in the adsorbed state. It is also necessary to specify the type of packing, which determines the distribution of voids. Hence, we introduce the coefficient η , which shows the proportion of

filled space. The volume of the adsorption monolayer is given by the relation

$$V = \frac{4\pi}{3} [(R+d)^3 - R^3], \quad (3)$$

and the effective volume filled with the adsorbate molecules is $V\eta$. Then the number of the adsorption sites in the monolayer is estimated as $V\eta/v$, while the number per unit surface area n_0 is found by an additional division by the median monolayer area:

$$n_0 = \frac{V\eta}{4\pi v(R+d/2)^2}. \quad (4)$$

In the limit of large R for a flat adsorbent surface,

$$n_0|_{R \rightarrow \infty} \rightarrow \bar{n}_0 \equiv \frac{d\eta}{v}, \quad (5)$$

and then relation (4) can be simplified to the form

$$\frac{n_0}{\bar{n}_0} = \frac{R^2 d + R d^2 + d^3/3}{d(R+d/2)^2} = \frac{1 + \delta + \delta^2/3}{(1 + \delta/2)^2} \approx 1 + \frac{\delta^2}{12}, \quad (6)$$

where $\delta \equiv d/R$ is a small parameter. Expression (6) shows that if the nano-adsorbent particle has a larger size, one can safely use adsorption relations for flat surfaces (the error is very low; even for $\delta = 1/3$, it is less than 1%).

Surfactants are adsorbed especially efficiently. Also, surfactants are related to our notion of protomicelle. When a nano-adsorbent molecule is coated by surfactant molecules or ions, it closely resembles a surfactant micelle with a solubilization core. This micelle-like particle acquired the name of protomicelle, which is encountered as frequently as a true micelle. Whereas the formation of true micelles requires a definite concentration of the surfactant solution (critical micelle concentration, CMC), protomicelles are formed at any concentration provided that the surfactant adsorption is positive (which is typically the case). In [4, 5], the term “protomicelle” has already been mentioned (although only once and without explanation). Probably, it has been used earlier in polymer chemistry; hence, to avoid misunderstanding, we will now use the term “adsorption protomicelle” (the word “protomicelle” used below should be understood this way).

In the theory of adsorption, the issue of adsorbent solubility is even not addressed, but this notion is natural for a nano-adsorbent. The solubility is the equilibrium concentration of a substance in a solution in contact with the pure phase of this substance (e.g., a solid precipitate); at a specified temperature, the chemical potential of the substance is constant. From the conditions $d\mu_i = 0$ and expressions (1) and (2), it follows that

$$kTd \ln a_i = d \sum_j u_j n_j, \quad (7)$$

where n_j is the number of adsorbed molecules (simultaneously it is the aggregation number of component j for protomicelles), the subscripts i and j refer to the nano-adsorbent and the adsorbate, respectively. The n_j value and the concentration of component j in solution c_j are related to the adsorption isotherm equation; in all cases, $dn_j/dc_j > 0$. Then relation (7) leads to the conclusion that the addition of the adsorbate (surfactant) to a solution always induces an increase in the activity and, hence, in the concentration, that is, in the solubility of the nano-adsorbent. The above theory demonstrates that the meaning of the term nano-adsorbent is not in the word by itself, but in the thermodynamic interpretation of this word.

While turning to the experiment, we would like to note, first of all, that early experiments involving nano-adsorbents and protomicelles were carried out for phthalocyanines [6, 7]. Now we use another dye, Nile red (NR; its chemical name is 9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one), the molecules of which are also planar (Fig. 1), hydrophobic, and poorly water-soluble (approximately 2 μM [8]). Studies of aqueous solutions of NR in combination with common ionic surfactants, tetradecyltrimethylammonium bromide [8] and sodium dodecyl sulfate [9], have already been carried out; and now it is time to switch to surfactants of a different type. In this study, nonanoic acid (NOA), exhibiting a series of transient properties, was used as the surfactant. First, this refers to a position between ionic and nonionic surfactants: NOA is a weak electrolyte and is adsorbed mainly in the non-dissociated form (the number of neutral molecules at the water–air interface in the adsorption layer is 272 times higher than the number of adsorbed NOA ions [10]). Second, this is intermediacy between colloidal (able to form micelles in this medium) and non-colloidal (those devoid of this ability) surfactants, although formally NOA refers to the former type and forms micelles in water at a concentration of less than 1 mM (according to figures given in [10]; below this concentration is defined more precisely).

The real aggregation number of NOA micelles is unknown, but using the Tanford procedure [11], we can calculate the theoretical aggregation number n as it was done previously (equation (25.6) [12–14]; the numbers in parentheses are in angstroms in the numerator and cubic angstroms in the denominator):

$$n = \frac{4\pi(1.5 + 1.265n_c)^3}{3(27.4 + 26.95n_c)}, \quad (8)$$

where n_c is the number of carbon atoms in the hydrocarbon tail of the surfactant molecule. In our case, $n_c = 8$, and relation (8) gives $n = 27.1$. This is the minimum possible NOA aggregation number, since relation (8) implies that each hydrocarbon substituent is wholly within the hydrocarbon core of the micelle.

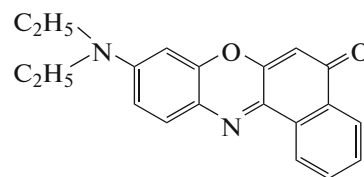


Fig. 1. Structural formula of Nile red.

Actually, surfactant molecules protrude from the micelle, which increases its real size. For example, in the case of a common surfactant, sodium dodecyl sulfate, this increase is approximately 1.3-fold. If this criterion is applied to our case, a NOA aggregation number of approximately 35 can be expected. The critical micelle concentration (CMC) of NOA is close to its solubility.

The NOA solubility requires a special comment. This refers to crystallization of a micellar solution, and it is not surprising that the data on the NOA solubility in water are highly scattered [15]. According to our estimate, at 30°C (our working temperature), the minimum solubility is approximately 1.65 mM. This makes NOA important for the study of pre-micellar solubilization and related protomicelles.

Here we studied the NOA–NR–water ternary system, where NOA functioned as the solubilizer, while NR is the solubilize. NOA and NR were commercial chemicals (Acros Organics) with 98% and 99% purity, respectively. Solutions for the study were prepared using distilled water with pH 6, measured on a Seven Multi (Mettler Toledo) instrument with an InLab Expert Pro pH combined electrode. The slightly acidic medium of distilled water is due to the absorption of carbon dioxide from air.

Spectrophotometric measurements were described previously [1, 8]. Traditionally [12–14], the solubilizer is considered to be the first component, while solubilize is taken as the second component; therefore, the concentrations of NOA and NR are designated by c_1 and c_2 , respectively. Then relation (7) can be written in the form:

$$kT \frac{d \ln a_2}{dc_1} = \frac{d(u_1 n_1)}{dc_1} \approx u_1 \frac{dn_1}{dc_1} > 0, \quad (9)$$

where n_1 and c_1 are related by the adsorption equation and always vary in parallel. The work of detachment of the hydrocarbon tail of the NOA molecule from the surface of the NR molecule, u_1 , is determined by hydrophobic interactions (i.e., properties of water) and, therefore, it does not depend on c_1 . According to the thermodynamic stability conditions, $da_2/dc_2 > 0$; hence, from inequality (9), it follows that

$$\frac{dc_2}{dc_1} > 0. \quad (10)$$

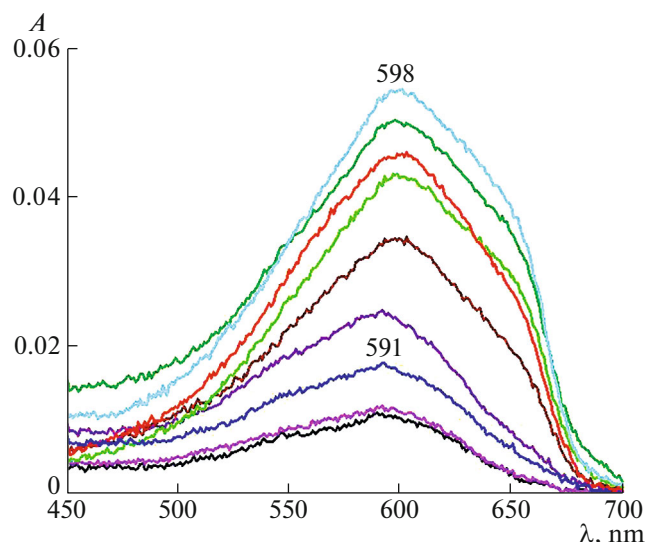


Fig. 2. Electronic absorption spectra of NR in saturated aqueous solutions in the presence of NOA with concentrations (from bottom to top), mM: 0.21, 0.3, 0.4, 0.5, 0.71, 0.9, 1, 1.23, and 1.42 at 30°C. A is absorbance, λ is the light wavelength. Optical path length $l = 5.07$ cm.

This means that the addition of NOA to a saturated solution of NR should increase the solubility of NR.

The strict fulfillment of this rule can be seen at the first glance in Fig. 2, which shows the spectra of NR in aqueous solutions (saturated with respect to NR) with different NOA concentrations. It can be seen that in the visible range of the NR spectrum, an increase in the NOA concentration induces a change in both the shape of the absorption band and the absorption intensity. At low c_1 values (0.21–0.4 mM), the position of the maximum ($\lambda = 591$ nm) and the shape of the band are typical of the monomeric state of NR in

water [6]. When $c_1 > 0.5$ mM, the A maximum in the spectra of NR (curves 5–9, from bottom to top) is red-shifted and is located at 598 nm wavelength. The left part of the band narrows down, and a shoulder appears at the right part, which is typical of protonated NR in an acid medium [16]. When there are not only NR monomers in water, but also NR aggregates (H-dimers formed upon stacking of the flat dye molecules), a second maximum, typical of dye dimers, appears at the short-wavelength side of the absorption spectrum (543 nm [9], 536 nm [16]). For the protonated NR molecules existing in acidic media (water + H_2SO_4 or ethanol + HCl), the absorption maxima (616 and 618 nm, respectively [16]) are located in the longer-wavelength spectral range than those for the neutral form (593 nm [8, 9, 18]). Thus, it can be suggested that at NOA concentrations $c_1 > 0.5$ mM, the dye in these systems occurs mainly in the protonated form.

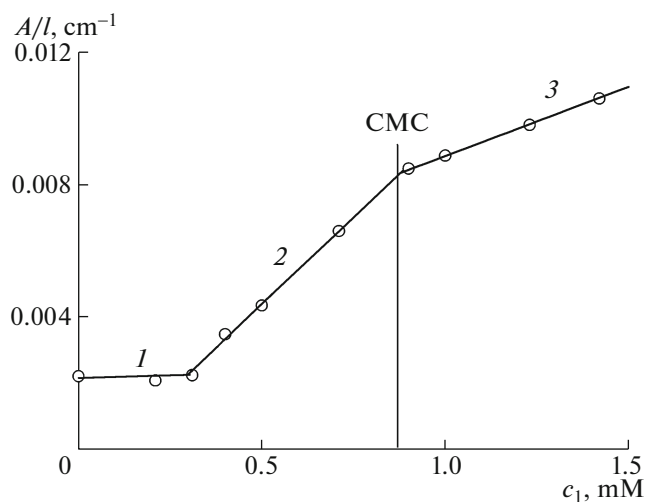


Fig. 3. Reduced (to $l = 1$ cm) absorbance of NR A/l vs. NOA concentration c_1 according to the spectral data shown in Fig. 2.

The maximum peak points of Fig. 2 are depicted in Fig. 3 as the dependence of the reduced (to the $l = 1$ cm length) absorbance A/l on the NOA concentration c_1 . The curve can be divided into three segments. Segment 1 is a weak dependence where the adsorption of NOA on the solid surface of NR is yet low and the detachment of NR molecules from the crystal is unlikely. In segment 2, the detachment has already started and protomices are being formed in the solution; in the absence of true micelles, protomices take on all the work on NR solubilization. Finally, segment 3 is characterized by the presence of micelles, which are also involved in NR solubilization, but to a lesser extent than protomices, as evidenced by a smaller slope of segment 3 compared to segment 2. This may be attributable to the fact that small NOA

micelles poorly absorb NR molecules and partially remain empty. Note that in previous studies [8, 9], the formation of protomicelles ended near CMC, and part 2 was absent. In this study, we encounter a unique case where NR protomicelles appear to be more important for the solubilization than micelles.

The junction of segments 2 and 3 (Fig. 3) forms a kink, which can be interpreted as the CMC of NOA. To more accurately find the point of kink and calculate the CMC, we will use the following technique. Segments 2 and 3 are approximated by equations (c_1 is expressed in millimoles per liter, mM; since the equations relate quantities with different units of measure, the numerical values also have units of measure):

$$A/l = 0.0108c_1 - 0.0009, \quad R^2 = 0.9977, \quad (11)$$

$$A/l = 0.0034c_1 + 0.0055, \quad R^2 = 0.9989, \quad (12)$$

where R^2 is the squared mixed correlation, reflecting the quality of approximation. The combined solution of equations (11) and (12) gives NOA CMC: $c_{1m} = 0.86$ mM. It is lower than that in pure water [10], but it has been proved that surfactant CMC always decreases in the presence of a solubilize [17].

In order to pass to the classic (micellar) solubilization curve $c_2(c_1)$, equation (12) should be divided by the NR extinction coefficient, ε_2 , which is unfortunately unknown for the NOA-containing aqueous system and is difficult to determine. In [18], $\varepsilon_2 = 3.31 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, found for NR in a mixture of dioxane and water, was used to calculate the solubilization capacity of Triton X-100. For a system with tetradecyltrimethylammonium bromide, we had $\varepsilon_2 = 2.713 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [8], while for a system containing sodium dodecyl sulfate, $\varepsilon_2 = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was used [9]. Therefore, for a rough estimation, we may use $\varepsilon_2 = 3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} = 30 \text{ mM}^{-1} \text{ cm}^{-1}$, which is close to all of the above values. By dividing equation (12) by this value, we get the equation for the solubilization curve as

$$c_2 \approx 0.0001c_1 + 0.00018, \quad (13)$$

where both concentrations are expressed in mM.

The coefficient at c_1 in equation (13) is equal to the solubilization capacity s of NOA micelles, which is the ratio of the aggregation numbers of the solubilize z and solubilizer n :

$$s \equiv \frac{z}{n} \approx 0.0001. \quad (14)$$

It can be seen from relation (14) that at $z = 1$ (each NOA micelle contains one solubilized NR molecule); the aggregation number n becomes unrealistically great. Obviously, average z must be much lower than unity, which means that only a small fraction of

micelles participates in solubilization. Note that in the micellar concentration region, protomicelles are indistinguishable from usual micelles with a solubilize; hence, it is quite possible that all of them originate from the protomicelles. Owing to the flat geometry of NR molecules, the latter look like disc-like micelles, whereas “empty” NOA micelles are spherical. It may happen that in the micellar region, too, the number of NR molecules in the solution increases via the protomicelle mechanism (adsorption of NOA molecules on the NR molecules as a nano-adsorbent). In any case, the role of NOA micelles in the NR solubilization is minor, while protomicelles play the crucial role.

Thus, it can be stated that the results of this study boost the importance of the protomicelle and nano-adsorbent concepts.

FUNDING

This study was supported by the Russian Foundation for Basic Research (project no. 20-03-00641) and was performed within the state assignment of the Ministry of Science and Higher Education of the Russian Federation (subject registration no. 122011300052-1).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Rusanov, A.I., Movchan, T.G., and Plotnikova, E.V. *Dokl. Phys. Chem.*, 2020, vol. 495, no. 2, pp. 181–185. <https://doi.org/10.1134/S0012501620120027>
2. Rusanov, A.I., *Colloids Surf., A*, 2021, vol. 629, p. 127453. <https://doi.org/10.1016/j.colsurfa.2021.127453>
3. Kuni, F.M. and Rusanov, A.I., *Theor. Math. Phys.*, 1970, vol. 2, p. 192.
4. Zhu, P.W. and Napper, D.H., *Colloids Surf., A*, 1996, vol. 113, pp. 145–153. [https://doi.org/10.1016/0927-7757\(96\)03520-0](https://doi.org/10.1016/0927-7757(96)03520-0)
5. El-Ejmi, A.A.S. and Huglin, M.B., *Eur. Polym. J.*, 1997, vol. 33, pp. 1281–1284. [https://doi.org/10.1016/S0014-3057\(96\)00272-8](https://doi.org/10.1016/S0014-3057(96)00272-8)
6. Movchan, T.G., Rusanov, A.I., and Plotnikova, E.V., *Colloid J.*, 2021, vol. 83, no. 3, pp. 356–364. <https://doi.org/10.1134/S1061933X21030121>
7. Movchan, T.G., Rusanov, A.I., and Plotnikova, E.V., *Colloid J.*, 2021, vol. 83, no. 4, pp. 468–473. <https://doi.org/10.1134/S1061933X21040062>
8. Movchan, T.G., Rusanov, A.I., and Plotnikova, E.V., *Russ J. Org. Chem.*, 2022, vol. 92, no. 10, pp. 2023–2032. <https://doi.org/10.1134/S1070363222100164>
9. Rusanov, A.I., Movchan, T.G., and Plotnikova, E.V., *Molecules*, 2022, vol. 27, p. 7667. <https://doi.org/10.3390/molecules27227667>

10. Badban, S., Hyde, A.S., and Phan, C.M., *ACS Omega*, 2017, vol. 2, pp. 5565–5573.
<https://doi.org/10.1021/acsomega.7b00960>
11. Tanford, Ch., *The Hydrophobic Effect. Micelles and Biological Membranes*, New York: Wiley, 1973.
12. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
13. Rusanov, A.I., *Micellization in Surfactant Solutions*, Reading, UK: Harwood Academic Publ., 1996. ISBN 90-5702-297-4
14. Rusanov, A.I. and Shchekin, A.K., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in surfactant solutions), 2nd ed., St. Petersburg: Lan', 2016.
15. Yalkowsky, S.H., He, Y., and Jain, P., *Handbook of Aqueous Solubility Data*, 2nd ed., London: CRC Press, 2010.
16. Selivanov, N.I., Samsonova, L.G., Artyukhov, V.Ya., and Kopylova, T.N., *Russ. Phys. J.*, 2011, vol. 54, no 5, pp. 601–606.
<https://doi.org/10.1007/s11182-011-9658-4>
17. Rusanov, A.I., *Colloid J.*, 2021, vol. 83, pp. 127–134.
<https://doi.org/10.1134/S1061933X20060113>
18. Kurniasih, I.N., Liang, H.P., Mohr, P.Ch., Khot, G., Rabe, J.P., and Mohr, A., *Langmuir*, 2015, vol. 31, pp. 2639–2648.
<https://doi.org/10.1021/la504378m>

Translated by Z. Svitanko

Publisher's Note. Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.